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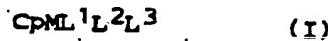
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Title of Invention: Catalyst for Olefin Polymerization and Method of Polyolefin Production with the Use of Said Catalyst

[Objective] To propose a catalyst for obtaining polyolefins which are highly copolymerizable, and characterized by high activity, narrow molecular weight dispersion and relatively broad compositional range, and a method of production of polyolefins which have the foregoing properties by using the said catalyst.

[Design] The invention concerns a catalyst which contains (A) a transition metal compound represented by Formula I:



(in which M may be Ti, Zr or Hf, Cp is a cyclic C₅₋₃₀ compound which has a cyclopentadienyl framework, and L¹, L² and L³ are 3 ligands), (B) an aluminoxy compound and (C) a phenolic compound; the invention also concerns a method of obtaining polyolefins by homopolymerization of a given olefin or copolymerization of olefin with some other olefin or a different polymerizable unsaturated compound with the use of the said catalyst.

Japanese Patent Disclosure H8-231622

Claims

1. Catalyst for olefin polymerization, consisting of

(A) Transition metal compound represented by the formula



(in which M may be titanium, zirconium or hafnium; Cp is a C₅-C₃₀ cyclic compound having a cyclopentadienyl framework with or without substitution; and L¹, L² and L³ are 6 ligands; they may or may not be all the same, but they should not bind with Cp to form a ring);

(B) Aluminoxane compound; and

(C) Phenolic compound.

2. Catalyst according to Claim 1 in which Component B may be a chain and/or ring type aluminoxane.

3. Catalyst according to Claim 1 in which Component C is a phenolic compound whose aromatic ring contains an OH group and C₁-C₂₀ hydrocarbon at the α and/or α' position.

4. A method of preparation of olefinic polymer by homopolymerization of olefin or copolymerization of olefin with some other olefin and/or some other polymerizable unsaturated compound.

5. Method according to Claim 4 in which the olefinic polymer is a copolymer of ethylene and α-olefin.

6. Method according to Claim 4 in which the olefinic polymer is polypropylene.

Detailed Description of the Invention

[industrial Utility] This invention concerns a catalyst for olefin polymerization and a method of preparation of polyolefins using the said catalyst. More specifically, the invention concerns a catalyst for the production of polyolefins characterized by excellent properties which include good copolymerizability, high activity per atom of aluminum and per transition metal, narrow polydispersity and relatively broad compositional distribution. The invention also concerns an efficient method of production of polyolefins, especially copolymers of ethylene and α -olefins and also polypropylenes, with the use of the said catalyst.

[Conventional Technology] Recently there has been a growing interest in agents consisting of metallocenes of transition metals and aluminoxane (Japanese Patent Disclosure S58-19309) as catalysts for olefin polymerization. The catalyst of that patent disclosure exhibits very high polymerization activity and relatively good copolymerizability, but had the drawbacks that a large amount of aluminoxane was needed and that copolymerizability was still somewhat inadequate. We therefore proposed, in an earlier document (Japanese Patent Disclosure H6-75691), the use of a catalyst containing a specific transition metal compound and aluminoxy compound in a prescribed molar ratio. That catalyst exhibited high activity relative to the aluminum content and excellent copolymerizability, but activity per unit transition metal was still inadequate. Moreover, the ethylene- α -olefin copolymer obtained with the use of catalyst consisting of metallocene of transitional metal and aluminoxane had a narrow molecular weight distribution but a narrow compositional distribution. The effect of these properties was that the polymer film improved in its heat-sealability and impact strength but resistance to tear was poor.

In an effort to overcome these drawbacks, we proposed (Japanese Patent Disclosure H6-172643) a specific ethylene polymer characterized by narrow polydispersity and relatively broad compositional distribution. Meanwhile a catalyst consisting of quaternary transition metal compound containing a cyclopentadienyl ring (actually a compound in which cyclopentadienyl ring and a ligand combine to form a ring; a so-called constrained geometric catalyst), and aluminoxane (International Patent Disclosure 93-13140). Polyolefins obtained with the use of this catalyst was again characterized by narrow compositional distribution.

[Problem Which This Invention Seeks to Solve] The objective of the present invention is to present a catalyst which would provide a polyolefin characterized by good copolymerizability, high activity relative to both aluminum and transition metal, narrow polydispersion and relatively wide compositional distribution. The invention also concerns a method by which polyolefins, especially ethylene/ α -olefin copolymer and polypropylene, are efficiently obtained with the use of the said catalyst.

[Method for Solving the Existing Problem] After intensive efforts to achieve our objective, we discovered that by combining a specific transition metal compound which has a cyclopentadienyl (substituted or unsubstituted) framework with aluminoxane compound and a phenolic compound, the desired type of catalyst is obtained, 5 and that by conducting homo- or copolymerization of olefins in the presence of the said catalyst, polyolefins, especially ethylene/ α -olefin copolymer and polypropylene having a narrow polydispersity and relatively broad compositional distribution could be obtained. The present invention is based on this observation. With this 10 invention, we propose a catalyst for polyolefin production in which the catalyst contains (A) a transition metal compound represented by Formula I:



(in which M may be Ti, Zr or Hf; Cp is a cyclic C₅-30 compound which has a cyclopentadienyl framework which makes a π -bonding with M by η^5 union; L¹, L² and L³ are 6 ligands which coordinate with M by σ -bonding. Examples of these ligands are R', OR', SR', SO₃R', NR'R'', PR'R'', NO₂, halogen, 1-pyrrolyl and 1-pyrrolidinyl. R' and R'' are C₁-20 hydrocarbons or hydrocarbon-containing silyls. At least one of them should be atomic halogen, OR', NR'R'' or PR'R''. It is even more preferable that all of the σ ligands should be halogen, since this results in stability on storage. L¹, L² and L³ may be all the same or different, but they must not combine with Cp to form a ring. If this happens, the compositional distribution of the polyolefin is narrowed and our stated objective will not be attained.

The cyclic C₅-30 group which has a substituted or unsubstituted cyclopentadienyl structure which coordinates with M by π bonding through a η^5 type union is a single entity. The substituents in the substituted cyclopentadienyl framework may bond with each other to form a new cyclic structure. Groups which have the indenyl, substituted indenyl, fluorenyl or substituted fluorenyl framework are included. As for R' and R'', the C₁-20 hydrocarbon may be alkyl, cycloalkyl, aryl or aralkyl. Examples of alkyls are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, or t-butyl, pentyl, hexyl, octyl, decyl or dodecyl; examples of cycloalkyls are cyclopentyl and cyclohexyl; examples of aryls are phenyl and tolyl; and examples of aralkyls are benzyl and phenethyl. Examples of hydrocarbon-containing silyls are trimethylsilyl and triphenylsilyl. Examples of OR' are alkoxy such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, t-butoxy, pentoxy, hexoxy, octoxy and cyclohexoxy; and aryloxy such as phenoxy. Examples of SR' are methylthio, ethylthio, cyclohexylthio and phenylthio. Examples of SO₃R' are alkylsulfonyls such as methanesulfonyl, ethanesulfonyl, n-propanesulfonyl, isopropanesulfonyl, n-butanesulfonyl, sec-butanesulfonyl, t-butanesulfonyl and isobutanesulfonyl; and Arylsulfonyl such as benzenesulfonyl. Examples

of NR'R" are dimethylamino, diethylamino, di(n-propyl)amino, diisopropylamino, di-(n-butyl)amin, diisobutylamino, di(sec-butyl)amino, dit-butyl)amino, dipentylamino, dihexylamino, dioctylamino, diphenylamino, dibenzylamino, methylethylamino, (t-butyl trimethylsilylamino and methyltrimethylsilylamino. Examples of PR'-R" are dimethylphosphide, diethylphosphide, di(n-propyl)phosphide, diisopropylphosphide, di-(n-butyl)phosphide, diisobutylphosphide, di(sec-butyl)phosphide, di(t-butyl)phosphide, dipentylphosphide, dihexylphosphide, dioctylphosphide, diphenylphosphide, dibenzylphosphide, methylethylphosphide, (t-butyl)trimethylsilylphosphide and methyltrimethylsilylphosphide. The atomic halogen may be F, Cl, Br or I.

10 The transition metal compound represented by Formula I may be cyclopentadienyltitanium trimethyl; cyclopentadienyltitanium triethyl; cyclopentadienyltitanium tri(n-propyl); cyclopentadienyltitanium triisopropyl; cyclopentadienyltitanium tri(n-butyl); cyclopentadienyltitanium triisobutyl; cyclopentadienyltitanium tri(s-butyl); cyclopentadienyltitanium tri(t-butyl); methylcyclopentadienyltitanium trimethyl; 1,2-dimethylcyclopentadienyltitanium trimethyl, 1,2,4-trimethylcyclopentadienyltitanium trimethyl; 1,2,3,4-tetramethylcyclopentadienyltitanium trimethyl; pentamethylcyclopentadienyltitanium trimethyl; pentamethylcyclopentadienyltitanium triethyl; pentamethylcyclopentadienyltitanium tri(n-propyl); pentamethylcyclopentadienyltitanium tri(n-butyl); pentamethylcyclopentadienyltitanium triisobutyl; pentamethylcyclopentadienyltitanium tri(s-butyl); pentamethylcyclopentadienyltitanium tri(t-butyl); cyclopentadienyltitanium trimethoxide; cyclopentadienyltitanium tri(n-propoxide); cyclopentadienyltitanium triisopropoxide; cyclopentadienyltitanium triphenoxide; methylcyclopentadienyltitanium trimethoxide; (n-butyl)cyclopentadienyltitanium trimethoxide; dimethylcyclopentadienyltitanium trimethoxide; dimethylcyclopentadienyltitanium triethoxide; dimethylcyclopentadienyltitanium tri(n-propoxide); dimethylcyclopentadienyltitanium triisopropoxide; dimethylcyclopentadienyltitanium triphenoxide; di(t-butyl)cyclopentadienyltitanium trimethoxide; di(t-butyl)cyclopentadienyltitanium triethoxide; di(t-butyl)cyclopentadienyltitanium tri(n-propoxide); di(t-butyl)cyclopentadienyltitanium triisopropoxide; di(t-butyl)cyclopentadienyltitanium triphenoxide; bis(trimethylsilyl)cyclopentadienyltitanium trimethoxide; bis(trimethylsilyl)cyclopentadienyltitanium triethoxide; bis(trimethylsilyl)cyclopentadienyltitanium tri(n-propoxide); bis(trimethylsilyl)cyclopentadienyltitanium triisopropoxide; bis(trimethylsilyl)cyclopentadienyltitanium triphenoxide; trimethylcyclopentadienyltitanium trimethoxide; trimethylcyclopentadienyltitanium triethoxide; trimethylcyclopentadienyltitanium tri(n-propoxide); trimethylcyclopentadienyltitanium triisopropoxide.

propoxide; trimethylcyclopentadienyltitanium triphenoxide; triethylcyclopentadienyltitanium trimethoxide; [bis(dimethylsilyl)methyl]cyclopentadienyltitanium trimethoxide; [di(t-butyl, methyl)cyclopentadienyltitanium triethoxide; tetramethylcyclopentadienyltitanium trimethoxide; tetramethylcyclopentadienyltitanium tri(n-propoxide); tetramethylcyclopentadienyltitanium triisopropoxide; tetramethylcyclopentadienyltitanium tri(n-butoxide); tetramethylcyclopentadienyltitanium tri(sec-butoxide); tetramethylcyclopentadienyltitanium tri(t-butoxide); tetramethylcyclopentadienyltitanium triphenoxide; [tetramethyl, 4-methoxyphenyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, 4-methoxyphenyl]cyclopentadienyltitanium triethoxide; [tetramethyl, 4-methoxyphenyl]cyclopentadienyltitanium triisopropoxide; [tetramethyl, 4-methoxyphenyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, 4-methylphenyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, 4-methylphenyl]cyclopentadienyltitanium triethoxide; [tetramethyl, 4-methylphenyl]cyclopentadienyltitanium tri(n-propoxide); [tetramethyl, 4-methylphenyl]cyclopentadienyltitanium triisopropoxide; [tetramethyl, 4-methylphenyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, benzyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, benzyl]cyclopentadienyltitanium tri(n-propoxide); [tetramethyl, benzyl]cyclopentadienyltitanium triisopropoxide; [tetramethyl, benzyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, 2-methoxyphenyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, 2-methoxyphenyl]cyclopentadienyltitanium triethoxide; [tetramethyl, 2-methoxyphenyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, ethyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, ethyl]cyclopentadienyltitanium triethoxide; [tetramethyl, ethyl]cyclopentadienyltitanium triisopropoxide; [tetramethyl, ethyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, n-butyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, n-butyl]cyclopentadienyltitanium triethoxide; [tetramethyl, n-butyl]cyclopentadienyltitanium tri(n-propoxide); [tetramethyl, n-butyl]cyclopentadienyltitanium triisopropoxide; [tetramethyl, n-butyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, phenyl]cyclopentadienyltitanium triethoxide; [tetramethyl, phenyl]cyclopentadienyltitanium triphenoxide; [tetramethyl, trimethylsilyl]cyclopentadienyltitanium trimethoxide; [tetramethyl, trimethylsilyl]cyclopentadienyltitanium triphenoxide; pentamethylcyclopentadienyltitanium trimethoxide; pentamethylcyclopentadienyltitanium triethoxide; pentamethylcyclopentadienyltitanium tri(n-propoxide); pentamethylcyclopentadienyltitanium triisopropoxide; pentamethylcyclopentadienyltitanium tri(n-butoxide); pentamethylcyclopentadienyltitanium triisobutoxide; pentamethylcyclopentadienyltitanium tri(s-but-

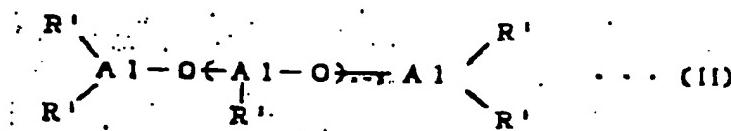
oxide); pentamethylcyclopentadienyltitanium tri(*t*-butoxide); pentamethylcyclopentadienyltitanium tri(cyclohexoxide); pentamethylcyclopentadienyltitanium triphenoxide; cyclopentadienyltitanium triphenoxide; cyclopentadienyltitanium tribenzyl; indenyltitanium trimethoxide; indenyltitanium triethoxide; indenyltitanium trimethyl; indenyltitanium tribenzyl; cyclopentadienyltitanium tri(methanesulfonyl); trimethylcyclopentadienyltitanium (tribenzenesulfonyl); tetramethylcyclopentadienyltitanium tri(ethanesulfonyl); pentamethylcyclopentadienyltitanium tri(methanesulfonyl); cyclopentadienyltitanium tris(dimethylamide); trimethylcyclopentadienyltitanium tris(dimethylamide); pentamethylcyclopentadienyltitanium tris(dimethylamide); pentamethylcyclopentadienyltitanium tris(dibenzylamide); pentamethylcyclopentadienyltitanium tris(diethylamide); cyclopentadienyltitanium tri(nitro); or pentamethylcyclopentadienyltitanium tri(nitro). The above compounds in which the metal is zirconium or hafnium instead of titanium may also be used.

Other examples are cyclopentadienyltitanium dimethyl monochloride; cyclopentadienyltitanium monoethyl dichloride; cyclopentadienyltitanium di(*n*-propyl) nobo-chloride; cyclopentadienyltitanium diisopropyl monochloride; cyclopentadienyltitanium di(*n*-butyl) monochloride; cyclopentadienyltitanium diisobutyl monochloride; cyclopentadienyltitanium di(*s*-butyl) monochloride; cyclopentadienyltitanium di(*t*-butyl) monochloride; 1,2-dimethylcyclopentadienyltitanium dimethyl monochloride; 1,2,4-trimethylcyclopentadienyltitanium dimethyl monochloride; 1,2,3,4-tetramethylcyclopentadienyltitanium dimethyl monochloride; pentamethylcyclopentadienyltitanium dimethyl monochloride; cyclopentadienyltitanium monochloro-dimethoxide; cyclopentadienyltitanium dichloro-dimethoxide; cyclopentadienyltitanium dichloromonochloride; cyclopentadienyltitanium monochloro-(*n*-propoxide); cyclopentadienyltitanium monochloro-diisopropoxide; cyclopentadienyltitanium monochloro-diphenoxide; dimethylcyclopentadienyltitanium monochloro-dimethoxide; dimethylcyclopentadienyltitanium monochloro-diethoxide; dimethylcyclopentadienyltitanium monochloro-di(*n*-propoxide); dimethylcyclopentadienyltitanium monochloro-diphenoxide; bis(trimethylsilyl)cyclopentadienyltitanium monochloro-dimethoxide; trimethylcyclopentadienyltitanium monochloro-diphenoxide; triethylcyclopentadienyltitanium monochloro-dimethoxide; [bis(dimethylsilyl),methyl]-cyclopentadienyltitanium monochloro-dimethoxide; tetramethylcyclopentadienyltitanium monochloro-dimethoxide; tetramethylcyclopentadienyltitanium monochloro-di(*n*-butoxide); tetramethylcyclopentadienyltitanium monochloro-diisobutoxide; tetramethylcyclopentadienyltitanium monochloro-di(*s*-butoxide); tetramethylcyclopentadienyltitanium monochloro-di(*t*-butoxide); tetramethyl,4-methoxyphenyl)cyclopentadienyl-

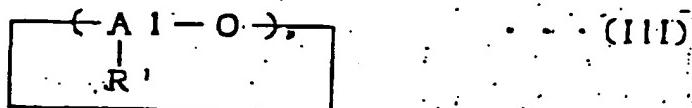
titanium monochloro-dimethoxide; [tetramethyl,4-methylphenyl]cyclopentadienyltitanium monochloro-dimethoxide; [tetramethyl,benzyl]cyclopentadienyltitanium monochloro-dimethoxide; [tetramethyl,benzyl]cyclopentadienyltitanium monochloro-diphenoxide; [Tetramethyl,2-methoxyphenyl]cyclopentadienyltitanium monochloro-dimethoxide; [tetramethyl,ethyl]cyclopentadienyltitanium monochloro-dimethoxide; [tetramethyl,ethyl]cyclopentadienyltitanium monochloro-diethoxide; [tetramethyl,n-butyl]cyclopentadienyltitanium monochloro-diethoxide; [tetramethyl,n-butyl]cyclopentadienyltitanium monochloro-di(n-propoxide); [tetramethyl,n-butyl]cyclopentadienyltitanium monochloro-diisopropoxide; [tetramethyl,phenyl]cyclopentadienyltitanium monochloro-dimethoxide; [tetramethyl,trimethylsilyl]cyclopentadienyltitanium monochloro-dimethoxide; pentamethylcyclopentadienyltitanium dichloro-monomethoxide; pentamethylcyclopentadienyltitanium monochloro-diethoxide; pentamethylcyclopentadienyltitanium monochloro-di(cyclohexoxide); pentamethylcyclopentadienyltitanium monochloro-diphenoxide; indenyltitanium monochloro-dimethoxide; cyclopentadienyltitanium monochloro-di(methanesulfonyl); pentamethylcyclopentadienyltitanium monochloro-bis(diethylamide); pentamethylcyclopentadienyltitanium monochloro-bis[di(n-butyl)amide]; pentamethylcyclopentadienyltitanium dichloro(dimethylamide); pentamethylcyclopentadienyltitanium dichloro(diphenylamide); pentamethylcyclopentadienyltitanium dichloro(methylethylamide); pentamethylcyclopentadienyltitanium dichloro(t-butyltrimethylsilylamine); pentamethylcyclopentadienyltitanium dimethoxy(diphenylamide); pentamethylcyclopentadienyltitanium monochloro-bis(diethyl phosphide); pentamethylcyclopentadienyltitanium monochloro-bis[di(n-butyl)phosphide]; pentamethylcyclopentadienyltitanium dichloro(dimethyl phosphide); pentamethylcyclopentadienyltitanium dimethoxy(dimethyl phosphide); pentamethylcyclopentadienyltitanium dichloro(diphenylphosphide); pentamethylcyclopentadienyltitanium dichloro(methylethyl phosphide); pentamethylcyclopentadienyltitanium dichloro(t-butyltrimethylsilyl phosphide); pentamethylcyclopentadienyltitanium dimethoxy(diphenyl phosphide); cyclopentadienyltitanium trichloride; n-butylcyclopentadienyltitanium trichloride; tetramethylcyclopentadienyltitanium trichloride; pentamethylcyclopentadienyltitanium trichloride; [tetramethyl,n-butyl]cyclopentadienyltitanium trichloride; tetraisopropylcyclopentadienyltitanium trichloride; tetraphenylcyclopentadienyltitanium trichloride; norbornacyclopentadienyltitanium trichloride; indenyl titanium trichloride; 4,5,6,7-tetrahydroindenyl titanium trichloride; 1,2,3-trimethyl,4,5,6,7-tetrahydroindenyl titanium trichloride; [1,2,3,-4,5,6,7heptamethyl]indenyl titanium trichloride; pentamethylcyclopentadienyltitanium trifluoride; pentamethylcyclopentadienyltitanium tribromide and pentamethylcyclopentadienyl titanium triiodide. In place of titanium, zirconium or hafnium may

be used in these compounds. In the catalyst of this invention, Component A (transition metal compound) may be a single species or may be a combination of 2 or more.

Component B of this invention, the aluminoxane compound, is represented by Formula III:



(in the above formula, R' represents C_{1-20} , preferably C_{1-12}), alkyl, alkenyl, aryl or aryl-alkyl which may or may not be the same (e.g., there may be multiple hydrolysates of alkylaluminum); s is the level of polymerization and is usually 2-50, preferably 3-40); or it may be a substance represented by Formula III:



In Formula III, R' has been defined earlier; and p is the level of polymerization which is usually 3-50, preferably 7-40. The aluminoxane may be prepared by bringing together alkyl aluminum with a condensing agent such as water. There is no rigid specification as to procedure; any established method may be used. The following are examples: (1) organoaluminum compound is dissolved in organic solvent and brought into contact with water; (2) organoaluminum compound is added at the time of polymerization, with subsequent addition of water; (3) water of crystallization or water adsorbed to inorganic or organic substance is allowed to react with organoaluminum compound; and (4) trialkyldialuminoxane is allowed to react with trialkylaluminum and then with water. The aluminoxane may be insoluble in toluene.

The aluminoxanes may be categorized as follows:

- (a) Alkylaluminoxane prepared from a single alkylaluminum (organoaluminum, such as methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, s-butyl and t-butyl-aluminoxanes).
- (b) Alkylaluminoxane mixture prepared from two or more alkylaluminoxanes made as indicated in (a) and a mixture of prescribed proportionality is made.
- (c) Alkylaluminoxane copolymer obtained by mixing in prescribed proportion two or more alkylaluminum (organoaluminum) compounds made according to any of methods 1-4; Examples are methyl-ethylaluminoxane, methyl-n-propylaluminoxane, methyl-isopropyl-aluminoxane, methyl-n-butylaluminoxane; methyl-isobutylaluminoxane; ethyl-n-propyl-aluminoxane; ethyl-isopropylaluminoxane and ethyl-n-butylaluminoxane. The aluminoxanes may be used singly or in mixture. Alkylaluminoxanes are especially suitable. The aluminoxane obtained in this manner may retain some of the starting alkylaluminum

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as an impurity, but this is permissible.

Component C or phenolic compound is used in the catalyst of our invention for the purpose of further increasing the catalytic activity and copolymerizability. The phenolic compound typically is a substance in which the hydrogen attached to an aromatic ring such as a benzene ring or naphthalene ring has been substituted by at least one OH or OH plus at least one substituent other than OH. Examples of substituents other than OH are R², OR², SR², NR²R³; halogen or nitro. R² and R³ are C₁-20 hydrocarbons, represented by alkyl, cycloalkyl, aryl and aralkyl. Examples of alkyl are methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, octyl, decyl and dodecyl. Cycloalkyls include cyclopentyl and cyclohexyl; aryls include phenyls and tolyls; and aralkyls include benzyls and phenethyls. Specific examples of OR² are methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, t-butoxy, pentoxy, hexoxy, octoxy and cyclohexoxy, as well as aryloxys including phenoxy. Specific examples of NR²R³ are dimethylamino, diethylamino, di(n-propyl)amino, diisopropylamino, di(n-butyl)amino, diisobutylamino, di(sec-butyl)amino, di(t-butyl)amino, dipentylamino, dihexylamino, dioctylamino, diphenylamino, and dibenzylamino. The halogen may be chlorine, bromine, iodine or fluorine.

Component C should preferably be a phenolic compound with substitution by C₁-20 hydrocarbon, especially one in which the 'alpha' position of the OH has been replaced by C₁-20 hydrocarbon. Specific examples are phenol, 2-methylphenol, 2-ethylphenol, 2-n-propylphenol, 2-isopropylphenol, 2-n-butylphenol, 2-sec-butylphenol, 2-t-butylphenol, 3-t-butylphenol, 4-t-butylphenol, 4-t-octylphenol, 2-n-dodecylphenol, 2-phenylphenol, 4-phenylphenol, 2,6-dimethylphenol, 2,6-diethylphenol, 2,6-di-t-butylphenol, 2,4-di-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2-t-butyl-6-methylphenol, 2-n-dodecyl-4-methylphenol, 4-n-dodecyl-2-methylphenol, 2,6-diphenylphenol, 2,6-di-t-butyl-4-methoxyphenol, 2,6-di-t-butyl-4-ethylphenol, 2,4,6-tri-t-butylphenol, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-butyldienebis(6-t-butyl-m-cresol), 4,4'-thiobis(6-t-butyl-m-cresol), α -naphthol, β -naphthol, 2-fluorophenol, 3-fluorophenol, 4-fluorophenol, 2,4-difluorophenol, 2,5-difluorophenol, 2,6-difluorophenol, 2-methoxyphenol, 3-methoxyphenol, 4-methoxyphenol, 2,6-di-t-butyl-4-methoxyphenol, N,N-dimethyl-3-aminophenol, N,N-diethyl-3-aminophenol, N,N-di-n-butyl-3-aminophenol, 2,6-di-t-butyl-4-dimethylaminophenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2-nitro-4-methylphenol, 3-nitro-4-methylphenol, 4-nitro-3-methylphenol, 5-nitro-2-methylphenol, catechol, resorcinol, hydroquinone, 3-methylcatechol, 4-methylcatechol, 4-t-butylcatechol, 2-methylresorcinol, 5-methylresorcinol, methylhydroquinone, t-butylhydroquinone, 2,5-di-t-butylhydroquinone, 1,2-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 1,5-dihydroxynaphthalene.

ene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, pyrogallol, fluoroglucinol, 1,2,4-trihydroxybenzene, hexahydroxybenzene, 4,4'-thiobis(2,6-di-t-butylphenol) and 3,5-di-t-butyl-4-hydroxybenzyl chloride. The above may be used singly or in combination.

5 The proportionality between Component A and Component B should be such that the aluminum compound in Component B (expressed as atomic aluminum)/mols of transition metal compound in Component A is in the range of 1-10,000. When this molar ratio is less than 1, there is inadequate activity, and when the ratio exceeds 10,000, there is wastage of aluminoxy compound, in addition to which the material will be retained by the polymer in considerable amounts. In terms of activity, economy and product quality, the molar ratio should be in the range of 10-5,000, preferably 20-2,000.

10 15 The amount of Component C (phenolic compound) should be such that the molar ratio of OH in the phenol compound/aluminum in Component B is in the range of 0.005 to 0.8. If the molar ratio is under 0.005, activity and copolymerizability are insufficient, and if the ratio exceeds 0.8, both activity and copolymerizability are actually diminished. A good molar ratio range is 0.05-0.6, preferably 0.1-0.5. There is no requirement regarding the sequence of contact of the components, but for achieving optimal activity, B and C should be brought together first and then A should be added, or B and A should be combined followed by contact of C.

20 25 Other ingredients may be added within limits which would not interfere with the stated objective. Also, if desired, each catalytic component may be borne on a carrier, which may be an inorganic oxide such as silica or alumina, inorganic halide such as magnesium chloride, inorganic alkoxide such as diethoxymagnesium or a polymer such as polystyrene.

In the method of this invention, homopolymerization of olefin or copolymerization of olefin with some other olefin or polymerizable unsaturated material occurs in the presence of the catalyst prepared as described above. There is no special preference as to the kind of olefin; examples include α -olefins such as ethylene, propylene, butene-1, pentene-1, hexane-1, heptene-1, octane-1, nonane-1, decane-1, 4-phenylbutene-1, 6-phenylhexene-1, 3-methylbutane-1, 4-methylpentane-1, 3-methylbutene-1, 3-methylhexene-1, 4-methylhexene-1, 5-methylhexene-1, 3,3-dimethylpentene-1, 3,4-dimethylpentene-1, 4,4-dimethylpentene-1, 3,5,5-trimethylhexane-1 and vinylcyclohexane; and halo-substituted α -olefins such as hexafluoropropene, tetrafluoroethylene, 2-fluoropropene, fluorostyrene, 1,1-difluoroethylene, 3-fluoropropene, trifluorostyrene and 3,4-dichlorobutene-1. Other olefins for copolymerization may be selected from the foregoing list. One to two or more olefins in combination may be used.

Examples of polymerizable unsaturated compounds for copolymerization with olefin are cyclic diolefins, chain conjugated diolefins, chain unconjugated diolefins, aromatic vinyl compounds, unsaturated esters, lactones, lactams and epoxides. Specific examples of cyclic olefins are cyclopentene, cyclohexene, norbornene, 5-methylnorbornene, 5-ethylnorbornene, 5-propynorbornene, 5,6-dimethylnorbornene, 1-methylnorbornene, 7-methylnorbornene, 5,5,8-trimethylnorbornene, 5-phenylnorbornene and 5-benzylnorbornene. Examples of cyclic diolefins are 5-ethylideneborbornene, 5-vinylnorbornene, dicyclopentadiene and norbornadiene.

Specific examples of chain conjugated diolefins are 1,3-butadiene and isoprene. Those of chain unconjugated diolefins are 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, and 5-methyl-1,4-heptadiene which are 1,4-dienes; 1,5-hexadiene, 3-methyl-1,5-hexadiene, 3-ethyl-1,5-hexadiene, 3,4-dimethyl-1,5-hexadiene, 1,5-heptadiene, 5-methyl-1,5-heptadiene, 6-methyl-1,5-heptadiene, 1,5-octadiene, 5-methyl-1,5-octadiene and 6-methyl-1,5-octadiene which are 1,5-dienes; 1,6-octadiene, 6-methyl-1,6-octadiene, 7-methyl-1,6-octadiene, 7-ethyl-1,6-octadiene, 1,6-nona-diene, 7-methyl-1,6-nona-diene and 4-methyl-1,6-nona-diene which are 1,6-dienes; 1,7-octadiene, 3-methyl-1,7-octadiene, 3-ethyl-1,7-octadiene, 3,4-dimethyl-1,7-octadiene, 3,5-dimethyl-1,7-octadiene, 1,7-nona-diene and 8-methyl-1,7-nona-diene which are 1,7-dienes; 1,11-dodecadiene; and 1,13-tetradecadiene.

Examples of aromatic vinyl compounds begin with styrene and α -methylstyrene and continue with alkyl- or arylstyrenes such as p-methylstyrene, m-methylstyrene, o-methylstyrene, p-t-butylstyrene and p-phenylstyrene; alkoxystyrenes such as p-methoxystyrene, m-methoxystyrene, p-ethoxystyrene, p-n-propoxystyrene and p-n-butoxy-styrene; halogenated styrenes such as p-chlorostyrene, p-bromostyrene and p-iodostyrene; alkyl- or aryl-containing silylstyrenes such as p-trimethylsilylstyrene, m-trimethylsilylstyrene, o-trimethylsilylstyrene, p-dimethylphenylsilylstyrene, p-methyldiphenylsilylstyrene and p-triphenylsilylstyrene; halogenated silylstyrenes such as p-dimethylchlorosilylstyrene, p-methyldichlorosilylstyrene and p-trichlorosilylstyrene; alkenylstyrenes such as p-(2-propenyl)styrene, m-(2-propenyl)styrene, o-(3-butenyl)styrene and p-(3-butenyl)- α -methylstyrene; vinylphenyls such as 4-vinylphenyl, 3-vinylbiphenyl and 2-vinylbiphenyl; vinylphenylnaphthalenes such as 1-(4-vinylphenyl)naphthalene, 2-(3-vinylphenyl)naphthalene; vinylphenyl anthracenes such as 1-(4-vinylphenyl)anthracene and 2-(4-vinylphenyl)anthracene; vinylphenyl phenanthrenes such as 1-(4-vinylphenyl)phenanthrene and 2-(4-vinylphenyl)phenanthrene; and vinylphenyl pyrenes such as 1-(4-vinylphenyl)pyrene and 2-(4-vinylphenyl)pyrene.

Examples of unsaturated esters are ethyl acrylate and methyl methacrylate; examples of lactones are β -propiolactone, γ -butyrolactone and δ -butyrolactone;

examples of lactams are ϵ -caprolactam and δ -valerolactam; and examples of oxides are epoxipropane and 1,2-epoxybutane. The unsaturated compounds may be used singly or in combination, perhaps with other α -olefins named earlier.

There is no rigid specification regarding the procedure of polymerization; slurry-, high-temperature solution-, vapor phase- or bulk polymerization may be used. When solvent is used, it may be an inert substance such as C₅-18 aliphatic or alicyclic hydrocarbon or C₆-20 aromatic hydrocarbon. Specific examples are n-pentane, isopentane, hexane, heptane, octane, nonane, decane, tetradecane, cyclohexane, benzene, toluene, xylene and ethylbenzene. These may be used singly or in combination. There is no specification regarding the polymerization temperature, but it is usually 0-350°C, preferably 20-250°C. Neither is there any specification regarding the polymerization pressure, but it is usually 0-150 kg/cm²G, preferably 0-100 kg/cm²G. The duration of polymerization is usually from 5 minutes to 10 hours. The molecular weight may be adjusted by the kind and amount of catalytic components, temperature, and the presence of hydrogen. The polyolefin obtained under these conditions have a narrow polydispersity and relatively broad compositional distribution, which are characteristics not ordinarily seen in polymers. The method of our invention is especially suited for the preparation of copolymers of ethylene and -olefins and polypropylenes.

[Examples] The invention is now described in further details by the use of examples. The scope of the invention is not limited to these examples.

Japanese Patent Disclosure H8-231622 (Examples only)

Table 1.

	Component C Compound	Amount (mmol)	Polymeriza- tion activity (kg/gTi)	Limiting viscosity (η)		Density (g/ml)
				(dl/g)	(dL/g)	
Example 1	2,6-di-t-butylphenol	0.2	234	5.2	0.908	
		0.1	140	5.8	0.907	
		0.1	148	5.2	0.912	
		0.5	144	6.2	0.900	
		0.03	48	5.0	0.915	
		—	9	5.8	0.916	
Control 1	t-Butanol	0.3	0	—	—	
" 2						

Example 1

A dry, 1-liter polymerizer provided with a stirring device was purged with dry nitrogen; after which 390 ml of dry n-hexane and 10 ml of 1-octene were added.

This was followed by the addition of 0.2 mmol of 2,6-di-t-butylphenol (Component C), 1.0 mmol of methyl aluminoxane (made by Albemarle Co.) (component B; expressed as mmol atomic Al), and 1.0 micromol of pentamethylcyclopentadienyl titanium trimethoxide (Component A), added in that order. The temperature was raised to 80°C and ethylene gas was led in. Pressure was maintained at 8 kg/cm² and polymerization was conducted at 80°C for 30 minutes. At the end of polymerization, pressure was released promptly and polymerization was ended by the addition of methanol. The content of the polymerizer was tossed into an excess of methanol-HCl mixture to decarbonize. The polymer was filtered and dried for 4 hours at 80°C to obtain 11.2 g of ethylene-1-octene. Activity was 234 kg per g Ti. The limiting viscosity (η) of this copolymer in decalin was 5.2 dl/g at 135°C and density was 0.908 g/ml.

Examples 2-5 and Controls 1, 2]

The procedure of Example 1 was followed except for varying the type and amount of Component C as indicated in Table 1. The results are shown in the table.

Example 6

The procedure in Example 1 was followed except for using 0.2 mmol of 2,6-di-t-butyl-4-methylphenol as Component C and conducting polymerization for 10 minutes. The amount of ethylene-1-octene copolymer obtained was 11.0 g. The data are shown in Table 2.

Examples 7-11 and Controls 3,4]

Aside from varying the type and amount of Component C, the procedure was the same as in Example 6. The results are shown in Table 2.

Table 2

	Component C	Polymerization activity (kg/gTi)	$[\eta]$ (dl/g)	Density (g/ml)
	Compound	Amt. (mmol)		
Example 6	2,6-di-t-butyl-4-methylphenol	0.2	229	6.8 0.800
Example 7	2,6-di-t-butyl-4-ethylphenol	0.2	243	6.7 0.889
Example 8	2,6-dimethylphenol	0.2	44	5.6 0.814
Example 9	2,6-diphenylphenol	0.2	69	6.8 0.812
Example 10	2-t-butylphenol	0.2	48	4.8 0.908
Example 11	Catechol	0.1	78	4.7 0.912
Control 3	Triphenylmethanol	0.2	4	— —
Control 4	Tetraethoxysilane	0.2	12	5.3 0.817

Example 12

The procedure in Example 1 was followed except that 390 ml of toluene was used as solvent and 2,6-di-t-butylphenol (0.1 mmol) was Component c. The amount of ethylene-1-octene copolymer was 10.6 g. The data are shown in Table 3.

Examples 13-21

The procedure in Example 12 was followed except for varying the type of Component A as indicated in Table 3. The results are shown in the table.

Table 3

	Component A	Activity (kg/gTi)	$[\eta]$ (dl/g)	Density (g/ml)
Example 12	Pentamethylcyclopentadienyltitanium trimethoxide	2.21	5.7	0.802
Example 13	Pentamethylcyclopentadienyltitanium tri(sec-butoxide)	3.89	5.5	0.899
Example 14	Pentamethylcyclopentadienyltitanium tri(cyclohexoxide)	3.06	5.8	0.801
Example 15	(Tetramethyl,n-butyl)cyclopentadienyltitanium trimethoxide	3.49	5.1	0.801
Example 16	Tetramethylcyclopentadienyltitanium trimethoxide	6.8	4.2	0.908
Example 17	Dimethylcyclopentadienyltitanium trimethoxide	8.8	3.0	0.807
Example 18	(n-Butyl)cyclopentadienyltitanium trimethoxide	8.2	2.4	0.915
Example 19	Pentamethylcyclopentadienyltitanium chloro(diethylamide)	2.91	5.0	0.897
Example 20	Pentamethylcyclopentadienyltitanium dichloro(diphenylamide)	6.51	5.0	0.801
Example 21	Pentamethylcyclopentadienyltitanium dichloro(t-butoxide)	1.25	5.2	0.898

Example 22

A dry, 1-liter polymerizer provided with a stirring device was purged with dry argon, and 460 ml of dry n-hexane, 40 ml of 1-octene, and 0.05N hydrogen were added. The temperature was raised to 150°C. As Component C, 1.2 mmols of 2,6-di-t-butylphenol; as Component B, 6.0 mmol (expressed as atomic Al) of methylaluminoxane; and as Component A, 10 μ mol of pentamethylcyclopentadienyltitanium trimethoxide were fed in along with ethylene gas. The partial pressure of ethylene was kept at 24 kg/cm² and polymerization was conducted at 150°C for 5 minutes. The process was promptly stopped by the addition of 15 ml of methanol. The content of the polymerizer was tossed into an excess of methanol, filtered, and dried under reduced pressure at 80°C for 4 hours to obtain 26.3 g of ethylene-1-octene copolymer. The limiting viscosity [η] in decalin at 135°C was 2.29 dl/g. The Mw/Mn determined by gel permeation chromatography (GPC) was only 2.2. The top of the peak obtained by DTA was 79°C, and the half-width was broad at 17.5°C. The methods of determinations were as follows.

(1) Determination of molecular weight distribution

Apparatus: Waters ALC/GPC: 150C

Column: TSK HM+GMH 6x2

Flow: 1.0 ml/min

Solvent: 1,2,4-trichlorobenzene

Under these conditions, Mw and Mn were found by GPC, and the ratio of Mw/Mn was calculated.

(2) Determination of compositional distribution

A column 10 mm in diameter and 250 mm in length was packed with Chromosorb PNAN (80/100 mesh) and polymer solution (concentration: about 6 g/liter at 135°C) was pumped in using a quantitative pump. This was cooled at a rate of 10°C per hour to the level of room temperature to allow the polymer to adsorb to the filler and crystallize. Next, o-dichlorobenzene was fed at a rate of .2 cc/min so that the rate of warming was 20°C/hr. The concentration of the eluted polymer was determined by means of an infrared detector-(1-AFox-Boro CVF Co.; CaF₂ cell) and compositional distribution curve relative to the elution temperature was prepared. In this manner, the position of the main peak temperature and the half value of the main peak were found.

Example 23

The procedure of Example 7 was followed but altering the order of contact of the catalytic components, as follows. The interior of a polymerizer (dry, 1-liter capacity) was purged with dry nitrogen, and 390 ml of dry n-hexane and 10 ml of 1-octene were added. Component B was 1.0 ml (expressed as atomic Al) of methylalumin-

oxane; Component A was pentamethylcyclopentadienyltitanium trimethoxide ($1.0 \mu\text{mol}$); and Component C was 0.2 mmol of 2,6-di-t-butyl-4-ethylphenol. The components were added in the above order. After the temperature had risen to 80°C , ethylene gas was introduced, and while the total pressure was maintained at $8 \text{ kg/cm}^2\text{G}$, polymerization was allowed to proceed at 80°C for 10 minutes. Upon termination of the polymerization, pressure was removed at once and methanol was added to the reactor. The content of the polymerizer was poured into an excess of a mixture of methanol and HCl to decarbonize. The polymer was filtered and separated, and dried under reduced pressure for 4 hours at 80°C to obtain 14.2 g of ethylene-1-octene copolymer. Activity was 296 kg/g Ti .

Example 24

The procedure was the same as in Example 6 except that Component A was $1.0 \mu\text{mol}$ of pentamethylcyclopentadienyltitanium dichloro(diphenylphosphide) and Component C was 0.2 mmol of 2,6-di-t-butylphenol. The amount of ethylene-1-octene copolymer obtained was 21.9 g; and activity was 457 kg/g Ti . The copolymer had a $[\eta]$ of 4.34 dl/g and density of 0.892 g/ml .

Example 25

Ethylene was copolymerized with norbornene. A dry, 1-liter polymerizer provided with a stirring device was purged with dry nitrogen, and 370 ml of dry n-hexane and 30 mmols of norbornene were added. Component C was 0.2 mmol of 2,6-di-t-butylphenol; Component B was 1.0 mmol (expressed as atomic Al) of methylalumininoxane; and Component A was pentamethylcyclopentadienyltitanium trimethoxide ($10 \mu\text{mols}$). These were added in the order given above. The temperature was raised to 70°C and ethylene gas was led in. Partial pressure of ethylene was kept at $6 \text{ kg/cm}^2\text{G}$ and polymerization was conducted for 30 minutes at 70°C . At the end of the process, pressure was relieved at once and methanol was added to the reactor. The content of the polymerizer was poured into an excess of methanol-HCl mixture to decarbonize. The polymer was filtered and separated, and dried under reduced pressure at 80°C for 4 hours, to obtain 35.0 g of ethylene-norbornene copolymer. Activity was 73 kg/g Ti . By DSC, no mp was observed, and the product was non-crystalline.

Control 5

A dry, 1-liter polymerizer was purged with dry argon, and 460 ml of dry n-hexane and 40 ml of 1-octene were added. The temperature was raised to 150°C . Next, 1.2 mmols of 2,6-di-t-butylphenol, 6.0 mmols (expressed as atomic Al) of methylalumininoxane and 5 umols of (t-butylamido)dimethyl(tetramethyl- γ^5 -cyclopentadienyl)-silanatitanium dichloride (restrictive geometric catalyst) were led in along with ethylene gas. Partial pressure of ethylene was kept at $24 \text{ kg/cm}^2\text{G}$ and polymerization was allowed to proceed for 10 minutes at 150°C . Polymerization was stopped at once

by the addition of 15 ml of methanol. The content of the polymerizer was poured into an excess of methanol. The polymer was filtered and dried under reduced pressure for 4 hours at 80°C to obtain 56.2 g of ethylene-1-octene copolymer. This had a $[\eta]$ of 2.7 dl/g in decalin at 135°C. Mw/Mn obtained by GPC was 5.3 which was broad, while the peak of compositional distribution curve was 80°C and the half-width was only 7.3°C.

Control 6

The procedure of Example 24 was followed except that 2,6-di-t-butylphenol (Component c) was not used. The amount of ethylene-norbornane was 0.49 g, activity was 1 kg/g Ti and mp by DSC was 119°C.

1-octene

Example 26

A dry, 1-liter reactor provided with a stirring device was purged with dry nitrogen, and 390 ml of dry n-hexane and 10 ml of 1-octene were added. Component C was 0.2 mmol of 2,6-di-t-butylphenol, Component B was 1.0 mmol (expressed as aromatic Al) of methylaluminoxane, and Component A was 0.5 μ l of pentamethylcyclopentadienyltitanium trichloride, added in that order. The temperature was raised to 80°C and ethylene gas was introduced. The total pressure was maintained at 8 kg/cm² and polymerization was allowed to proceed for 30 minutes at 80°C. At the end of the process, pressure was relieved promptly, and polymerization was stopped by adding methanol to the reactor. The reaction product was tossed into an excess of methanol-HCl mixture. The polymer was dried under reduced pressure for 4 hours at 80°C to obtain 9.1 g of product. Activity was 380 kg/g Ti, the $[\eta]$ was 4.6 dl/g and density was 0.900 g/ml.

Examples 27-31

The procedure in Example 26 was followed except for making variations indicated in Table 4. The results are shown in the table.

Table 4

	Component A	Activity (kg/g-Ti)	(η) (dl/g)	Density (g/ml)
Example 26	Pentamethylcyclopentadienyltitanium trichloride	380	4.6	0.900
Example 27	Cyclopentadienyltitanium trichloride	13	-	-
Example 28	Methyltitanium trichloride	3.3	1.2	0.887
Example 29	1,2,3,4,5,6,7-Heptamethylindenyltitanium trichloride	233	4.8	0.895
Example 30	Pentamethylcyclopentadienyltitanium tribromide	432	3.7	0.894
Example 31	Pentamethylcyclopentadienyltitanium dichloroisopropoxide	478	3.7	0.902

Control 7

The procedure in Example 26 was followed except that Component C was omitted. The yield of ethylene-1-octene was no more than a trace amount.

Example 32

A dry, 1-liter polymerizer was purged with dry nitrogen, after which 400 ml of dry n-hexane was added. Component C was 0.2 mmol of 2,6-di-t-butylphenol, Component B was 1.0 mmol (expressed as atomic Al) of methyl aluminoxane, and Component A was 2 μ mol of pentamethylcyclopentadienyltitanium trimethoxide. The temperature was raised to 70°C and propylene gas was led in. The total pressure was kept at 6 kg/cm² and polymerization was conducted for 30 minutes at 70°C. The process was terminated by tossing the content of the polymerizer into an excess of methanol-HCl mixture. The product was filtered and dried under reduced pressure for 4 hours at 80°C to obtain 15.7 g of non-crystalline polypropylene. Activity was 164 g/g Ti. Mw determined by GPC was 14.4×10^4 and Mw/Mn was 2.3.

Example 33

The procedure was the same as in Example 32 except that Component A was penta-methylcyclopentadienyltitanium trichloride. Activity was 503 kg/g Ti, Mw was 13.9×10^4 , and Mw/Mn was 2.15.

Control 8

The procedure in Example 32 was followed except for omitting Component C, and 1.7 g of non-crystalline polypropylene was obtained. Activity was 1.8 kg/g Ti.

Reference Example 1

A dry, 1-liter polymerizer provided with a stirring device was purged with dry nitrogen, and 440 ml of dry toluene and 60 ml of 1-octene were added. Next, 5.0 mmol (expressed as atomic Al) of methyl aluminoxane (made by Toso-Akuzo Company) and 0.5 micromol of dicyclopentadienylzirconium dichloride were added in that order. The temperature was raised to 80°C, after which ethylene gas was led in, and while the total pressure was kept at 4 kg/cm², polymerization was conducted for 20 minutes at 80°C. Polymerization was halted by relieving the pressure and adding methanol to the polymerizer. The content of the polymerizer was poured into an excess of methanol-HCl mixture. Polymer was filtered and dried under reduced pressure for 4 hours at 80°C to obtain 59.3 g of ethylene-1-octene copolymer. Its $[\eta]$ was 1.47 dl/g and its density was 0.914 g/ml.

Reference Example 2

The procedure in Reference Example 1 was followed except that, after adding 5.0 mmols (expressed as atomic Al) of methyl aluminoxane, 1.0 mmol of 2,6-di-t-butylphenol and 0.5 micromol of dichloropentadienylzirconium dichloride were added in that order. The product was 39.8 g of ethylene-1-octene copolymer. $[\eta]$ was 2.14 dl/g and density was 0.922 g/ml.

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